

Appendix N

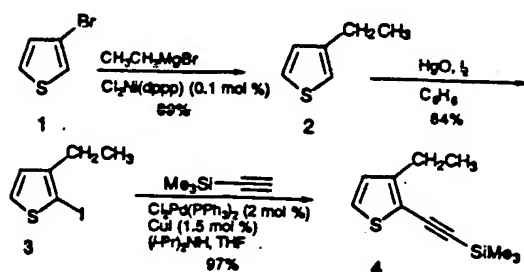
Potential Molecular Wires by an Iterative Doubling Approach. Doubling of Molecular Length at Each Iteration

Darren L. Pearson and James M. Tour*

Department of Chemistry and Biochemistry
University of South Carolina
Columbia, South Carolina 29208

The ultimate computational system would consist of logic devices that are ultra dense, ultra fast, and molecular sized.¹ Though bulk organic materials can indeed be semiconducting or even conducting,² electronic conduction based upon single or small packets or molecules has not been demonstrated and it is theoretically controversial.¹ Present nanopatterning techniques allow lithographic probe assemblies to be engineered down to the 100 Å gap regime.³ In an attempt to span this 100 Å gap with molecules and to assess the feasibility of molecular wire conduction, we describe here a new rapid synthetic approach to potential molecular wires based on oligo(thiophene-ethynylene) derivatives.^{4,5}

The synthesis of the key monomer 4, whose length will double at each stage is below.⁶ The iterative divergent/convergent synthetic approach is outlined in



Scheme 1. The sequence involves partitioning 4 into two portions; iodinating the 5-position in one of the portions to form 5 and protodesilylating the alkynyl end of the second portion to form 6. Bringing the two portions back together in the presence of a Pd/Cu catalyst 6c couples the aryl iodide to the terminal alkyne, thus generating the dimer 7. Iteration of this reaction sequence doubles the length of the dimer 7 to afford the tetramer 10, and so on to the octamer 13, and finally the 16-mer 16.

The optical spectra are interesting in that a near saturation of the systems appears to have occurred by the octamer stage so that doubling the conjugate length to the 16-mer caused little change in the absorbance maximum. The results of the size exclusion chromatography (SEC) are also quite intriguing. SEC is not a direct measure of molecular weight but a measure of the hydrodynamic volume. Thus by SEC using randomly coiled polystyrene standards, the number average molecular weights (M_n) of rigid rod polymers are usually greatly inflated relative to

the actual molecular weights (MW). Accordingly, the SEC recorded M_n values of the octamer (13) ($M_n=1610$, actual MW=1146) and 16-mer (16) ($M_n=3960$, actual MW=2220) were much greater than the actual MWs. Conversely, the monomer (4) through tetramer (10) had M_n values that were very close to the actual values because they are in the low MW region, prior to significant polystyrene coiling.

More recently developments in the area of "molecular wire" research has included the synthesis of a difunctionalized octamer with phenyl thioester end groups 19, an orthogonally fused 50 Å thiophene-ethynylene oligomer 20, and two monofunctionalized 16-mers with phenyl thioester end groups 21 and 22.^{7,8} These phenyl thioesters can be cleaved to thiols which have a strong affinity for gold. These thiols would then serve as "alligator clips" to hold the oligomers between gold electrodes for future studies.

Acknowledgments. We are grateful for support from the Office of Naval Research and the Advanced Research Projects Agency. Dr. Kevin Schey at the Medical University of South Carolina kindly obtained the laser desorption MS of 16. We also thank Molecular Design Ltd. for the use of their synthetic data base.

References and Notes

- (a) Bowden, M.J. In *Electronic and Photonic Applications of Polymers*; Bowden, M. J.; Turner, S.R., Eds.; (Advances in Chemistry, 218) American Chemical Society: Washington DC, 1988. (b) Farazdel, A.; Dupuis, M.; Clementi, E.; Aviram, A., *J. Am. Chem. Soc.* 1991, 113, 7064. (c) Tour, J. M.; Wu, R.; Schumm, J. S. *J. Am. Chem. Soc.* 1991, 113, 7064.
- Handbook of Conducting Polymers*; Skotheim, T.A., Ed.; Dekker: New York, 1986.
- Nanostructure Physics and Fabrication*; Reed, M. A.; Kirk, W. P., Eds.; Academic Press: San Diego, 1989.
- (a) Ignier, E.; Paynter, O.L.; Simmonds, D. J.; Whiting, M.C. *J. Chem. Soc., Perkin Trans. 1* 1987, 2447. (b) Zhang, J., Moore, J. S.; Xu, Z.; Aguirre, R. A. *J. Am. Chem. Soc.* 1992, 114, 2273. (c) Wegner, G. In *Thermoplastic Elastomers, A Comprehensive Review*, Legge, N.R.; Holden, G.; Schroeder, H.E.; Hasner, New York, 1987, 405.
- For a presentation of some foundational work in the area of "molecular wire", see: (a) Kenny, P. W.; Miller, L. L. *J. Chem. Soc., Chem. Commun.* 1988, 85. (b) Kugimiya, S.-i.; Lazrak, T.; Blanchard-Desce, M.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* 1991, 1179.
- (a) Tamao, K.; Kodama, S.; Nakajima, I.; Kumada, M.; Minato, A.; Suzuki, K. *Tetrahedron* 1982, 38, 3347. (b) Uhlenbroek, J. H.; Bijloo, J. D. *Recl. Trav. Chim. Pays-Bas* 1960, 79, 1181. (c) Suffert, J.; Ziessel, R. *Tetrahedron Lett.* 1991, 32, 757.
- The minimization was done using MMX with extended pi-Huckel and multiconformational parameters.
- Jones, L., II; Pearson, D.P.; Lamba, J.S.; Tour, J. M.; Whitesides, G.M.; Muller, C.J.; Reed, M.A. *Polymer Prep. (Am. Chem. Soc., Div. Polym. Chem.)* 1995, 36(1), 564.

